Depolarization ratio of the Raman modes of CO_2 gas and isovanillin aerosol*

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Depolarization ratios of the Raman modes of CO_2 gas and isovanillin aerosol have been measured using a 532 nm Raman system developed for detecting chemical gases and aerosols. The depolarization ratio of the 1285 and 1388 cm^{-1} modes of CO_2 have been determined to be 7 and 5%, respectively. The depolarization ratio of the 1116 and 1275 cm^{-1} modes of isovanillin have been determined to be 54%. Using the measured values of the depolarization ratio, the ratio of the off-diagonal and diagonal components of the Raman polarizability tensor have been deduced to be 26 and 22% for the 1285 and 1388 cm^{-1} modes of CO_2, respectively, and 73% for the 1116 and 1275 cm^{-1} modes of isovanillin.

Keywords: Depolarization ratio; Raman polarizability tensor components; CO_2; isovanillin;

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Introduction

In this paper, we report measurements of the depolarization ratio of the 1285 and 1388 cm^{-1} Raman modes of CO_2 gas and the 1116 and 1275 cm^{-1} modes of isovanillin aerosol. These Raman depolarization ratios are generally important for applications involving Raman spectroscopy of these materials. In particular, they are important for optimizing the performance of Raman systems aimed at detecting trace atmospheric gases and aerosols. A sensitive 532 nm Raman system (400-1400 cm^{-1}) developed for the detection of chemical aerosols and gases[1, 2] was used for the depolarization measurements. The measured values of the depolarization ratio have been used for a determination of the ratio of the off-diagonal and diagonal components of the Raman polarizability tensor for isovanillin aerosol and CO_2 gas. The Raman spectrum of the CO_2 gas was first reported by Dickinson et al.[3] The Raman cross sections of the 1285 and 1388 modes of CO_2 have previously been reported[4-6] as has been the depolarization of these modes[7, 8]. The Raman modes of isovanillin powder ($C_8H_8O_3$; CAS No. 621-59-0) have been previously reported[9] at 504, 1118, 1277, 1608, and 1671 cm^{-1} measured using 785 nm pump radiation. More recently, vibrational modes of isovanillin have been calculated using density functional theory.[10] To the best of our knowledge, this is the first report of the Raman depolarization ratio for any aerosol.

Experimental

Figure 1 shows a schematic of the 532 nm 10 W cw laser Raman system that was used for the measurement of the Raman scattering depolarization.[2] The pump laser propagates in the horizontal direction (z-axis) through the flow cell. The laser was polarized perpendicular to the direction of propagation (z-axis). The 532 nm half-wave plate (HWP) placed after the 45º-mirror was used to rotate the polarization from the vertical direction (y-axis) to the horizontal direction (x-axis). The Raman signal is collected along the x-axis.

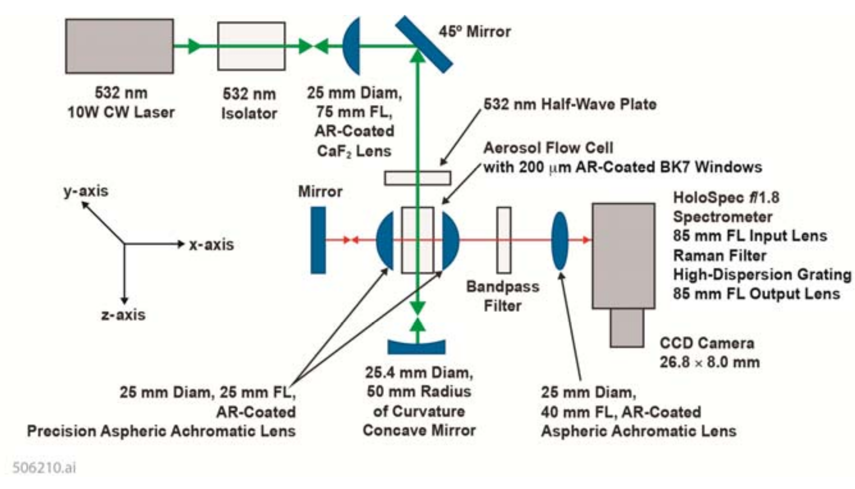

Figure 1. Schematic of the Raman system used for the measurement of chemical aerosols and gases.

The magnification M of the image of the laser focal spot on the spectrometer slit is 1.6, which is the ratio of the 40 mm focal length focusing lens and the 25 mm focal length collection lens. The diameter D of the laser focal spot, located in the center of the flow cell, was 50 μm. The spectrometer was sensitive to particles along a 3 mm length of the laser beam. The spectrometer grating diffraction efficiency was the same (within ±1%) for light polarization parallel and perpendicular to the plane of incidence.

The isovanillin aerosol was generated in a commercial blender in which the isovanillin powder was filled to just above the blender blades. A 1 to 5 second operation of the blender was sufficient to generate an aerosol of small isovanillin particles in the blender body.

Theoretical

Equation (1) shows the components of the 3x3 Raman polarizability tensor.

$$\alpha = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix}. \qquad (1)$$

For gases and aerosols (assuming random orientations) the tensor components must obey Eqs. (2) and (3).

$$\alpha_{xx} = \alpha_{yy} = \alpha_{zz,} \qquad (2)$$

and

$$\alpha_{xy} = \alpha_{yx} = \alpha_{yz} = \alpha_{zy} = \alpha_{zx} = \alpha_{xz}. \qquad (3)$$

The ratio of the horizontal laser polarization Raman signal (R_{HL}) to the vertical laser polarization Raman signal (R_{VL}) is given by

$$\beta = \frac{R_{HL}}{R_{VL}} = \frac{(\alpha_{yx})^2 + (\alpha_{zx})^2}{(\alpha_{yy})^2 + (\alpha_{zy})^2}. \qquad (4)$$

Using Eqs. (2) and (3), Eq. (4) may be written as

$$\beta = \frac{2(\alpha_{xy})^2}{(\alpha_{xx})^2 + (\alpha_{xy})^2}. \qquad (5)$$

The Raman depolarization ratio is given by

$$\rho = \frac{R_{perpendicular}}{R_{parallel}} = \frac{(\alpha_{xy})^2}{(\alpha_{xx})^2}, \tag{6}$$

where $R_{perpendicular}$ and $R_{parallel}$ are perpendicular and parallel components of the Raman signal. Combining Eqs. (5) and (6), the depolarization ratio may be expressed in the form

$$\rho = \frac{\beta}{2-\beta}, \tag{7}$$

which provides the method for the measurement of the Raman depolarization ratio. The ratio of off-diagonal and diagonal components of the Raman polarizability tensor is given by

$$\gamma = \frac{\alpha_{xy}}{\alpha_{xx}} = \sqrt{\rho}. \tag{8}$$

Results and Discussion

Figure 2 shows the Raman spectra of atmospheric CO_2 (~480 ppm) for vertical and horizontal laser polarizations obtained using 8.5 W laser power and 15 signal integration time. Using the values of $1.88\text{x}10^4$ and $1.473\text{x}10^5$ counts for the Raman signal for the horizontal and vertical polarization, respectively, for the 1285 cm^{-1} mode, we obtain a value of 13% for β, which yields a value of 7% for the depolarization ratio ρ for the 1285 cm^{-1} mode. Similarly, we obtain values of 9% for β and 5% for ρ for the 1388 cm^{-1} mode. Our values of 7% and 5% for ρ for the 1285 and 1388 cm-1 modes, respectively, are lower than the corresponding values of 18 and 14% reported previously. [8] However, the depolarization ratios reported in Ref. 8 were measured using *unpolarized* incident light, which does not yield the generally expected accepted definition of the depolarization ratio. The unpolarized incident/pump radiation depolarization ratio measured in Ref. 8 would be given by

$$\rho_u = \frac{2\rho}{1+\rho}. \tag{9}$$

For $\rho << 1$, ρ_u is approximately equal to 2ρ explains most of the discrepancy between our values of ρ and those of Ref. 8.

Substituting the above values of 7 and 5% for depolarization ratio in Eq. (7), we obtain values of 26 and 22% for γ for the 1285 and 1388 cm^{-1} modes of CO_2, respectively.

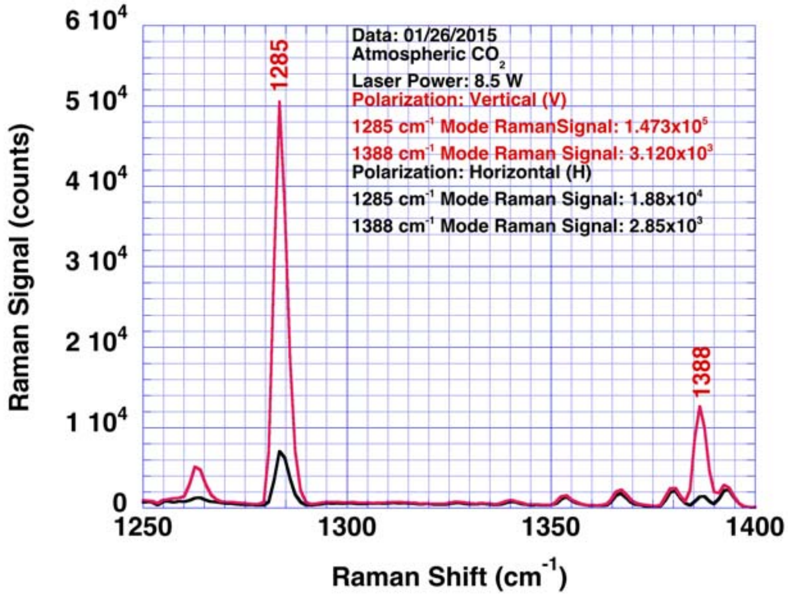

Figure 2. Raman spectra of atmospheric CO_2 (~ 480 ppm) for vertical (red curve) and horizontal (black curve) laser polarization obtained using 8.5 W laser power and 15 s Raman signal integration time.

Figure 3 shows the Raman spectra of isovanillin aerosol (~1.7ng/cm^3) for vertical and horizontal laser polarizations obtained using 8.5 W laser power and 2 s signal integration time.

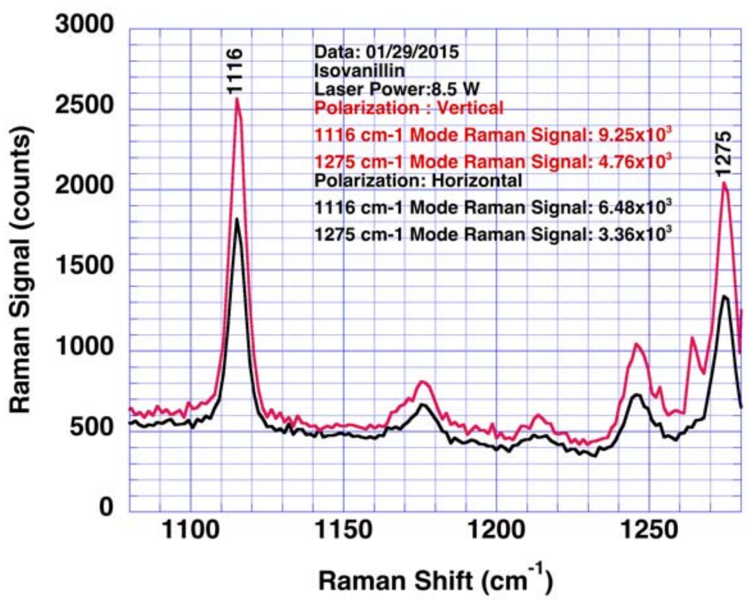

Figure 3. Raman spectra of isovanillin aerosol (~ 1.7 ng/cm^3) for vertical (red curve) and horizontal (black curve) laser polarization obtained using 8.5 W laser power and 2 s Raman signal integration time.

Using values of $9.25x10^3$ and $6.48x10^3$ counts for the Raman signal of the isovanillin 1116 cm^{-1} mode for the vertical and horizontal polarization, respectively, we obtain values of 70% for β and 54% for ρ for the 1116 cm^{-1} mode of isovanillin. Similarly, using values of $4.76x10^3$ and $3.36x10^3$ for Raman signal of the 1275 cm^{-1} mode, we obtain values of 70% for β and 54% for ρ for the 1275 cm^{-1} mode of isovanillin, which are same as for the 1116 cm^{-1} mode. To the best of our knowledge, this is the first report of depolarization ratio for a chemical aerosol.

Summary

We have measured values of 7 and 5%, respectively, for the depolarization ratio ρ of the 1285 and 1388 cm^{-1} Raman modes of CO_2. A value of 54% has been measured for ρ of the 1116 and 1275 cm^{-1} modes of isovanillin aerosol. The ratio γ of the off-diagonal and diagonal components of the 3x3 Raman polarizability tensor have been determined to be 26 and 22%, respectively, for the 1285 and 1388 cm-1 modes of CO_2 and 73% for the 1116 and 1275 cm^{-1} modes of isovanillin aerosol.

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